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(NASA-CR-157096) DEVELOPMENT AND EVALUATION  
OF DIE MATERIALS FOR USE IN THE GROWTH OF  
SILICON RIBBONS BY THE INVERTED RIBBON  
GROWTH PROCESS, TASK 2, LSSA PROJECT  
Quarterly Report (RCA Labs., Princeton, N. G3/37

N78-24553

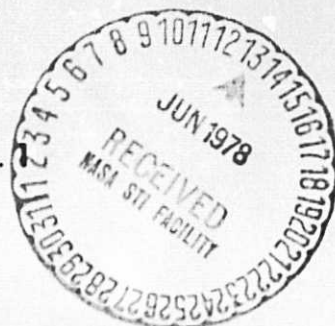
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## DEVELOPMENT AND EVALUATION OF DIE MATERIALS FOR USE IN THE GROWTH OF SILICON RIBBONS BY THE INVERTED RIBBON GROWTH PROCESS — TASK II — LSSA PROJECT

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Princeton, New Jersey 08540

QUARTERLY REPORT NO.

December 1977



This work was performed for the Jet Propulsion Laboratory,  
California Institute of Technology, under NASA Contract  
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Prepared Under Contract No. 954901 For  
JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
Pasadena, California 91103

# **DEVELOPMENT AND EVALUATION OF DIE MATERIALS FOR USE IN THE GROWTH OF SILICON RIBBONS BY THE INVERTED RIBBON GROWTH PROCESS — TASK II — LSSA PROJECT**

**M. T. Duffy, S. Berkman,  
G. W. Cullen, and H. I. Moss  
RCA Laboratories  
Princeton, New Jersey 08540**

## **QUARTERLY REPORT NO. 1**

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## PREFACE

This Quarterly Report No. 1, prepared by RCA Laboratories, Princeton, NJ 08540, describes work performed under Contract No. 954901 in the Materials and Processing Research Laboratory, H. Kressel, Director. G. W. Cullen is the Group Head and the Project Supervisor. M. T. Duffy is the Project Scientist. Others who participated in the research and/or writing of this report are S. Berkman, H. I. Moss, R. A. Soltis, H. E. Temple, J. F. Corboy, and M. Popov.

The JPL Project Monitor is T. O'Donnell.



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## SECTION I

### SUMMARY

Silicon sessile drop experiments were performed on a variety of commercially available refractory carbides, nitrides, oxides, and borides to examine the potential of these materials for applications involving either direct contact with molten silicon or as substrates for CVD coatings in the fabrication of dies and crucibles for containing molten silicon. Simultaneous experiments were also conducted with CVD layers of SiC,  $\text{Si}_3\text{N}_4$ , and  $\text{SiO}_x\text{N}_y$ . The latter two materials proved superior for purposes of contact with the silicon melt in relation to chemical reactivity and reduced impurity content.

Silicon nitride layers, deposited with  $\text{NH}_3:\text{SiH}_4$  ratios ranging from 100:1 down to 5:1, were examined in sessile drop experiments to determine if the layers are degraded as a result of using lower reagent ratios. The cost of ammonia (5 nines purity) at the higher ratios represents the major cost in the production of these layers, and a reduction in the above ratio could result in a substantial reduction in cost.

Preliminary experiments were undertaken on the stability of CVD  $\text{Si}_3\text{N}_4$  near the melting point of silicon. From our initial experiments it appears that the rate of decomposition is less than 100 Å/h just below the melting point of silicon.

Silicon ribbon segments were grown from vitreous carbon dies which had been coated with CVD  $\text{Si}_3\text{N}_4$ . Depending upon the purity of the die materials, ribbon resistivity values up to 40 Ω-cm were obtained.



## SECTION II

### INTRODUCTION

The objective of this program is to develop and evaluate die materials for use in the growth of silicon ribbons by the inverted ribbon growth process (IRG). The major emphasis is on developing CVD coatings of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_x\text{N}_y$  on suitable die materials and studying the stability and interaction of these layers with molten silicon. The dies will be tested in silicon ribbon growth experiments. The ribbon will be characterized electrically and crystallographically. Self-supporting CVD dies and crucibles will also be fabricated and deposition parameters will be adjusted where possible to favor minimum cost. Other potentially useful materials will be prepared and tested.



### SECTION III

#### PROGRESS AND TECHNICAL DISCUSSION

##### A. SESSILE DROP EXPERIMENTS WITH REACTION-SINTERED AND HOT-PRESSED MATERIALS

We have examined various refractory materials in silicon sessile drop experiments in order to ascertain the most suitable candidates for further study as die materials or substrates for CVD layers. The refractories included carbides, nitriles, and oxides, and were maintained in contact with molten silicon at 1440°C in ultrapure He for 30 min. A summary of our observations is presented in Table 1. Section micrographs are provided in those cases where total absorption or reaction did not occur and are presented in Appendix A.

Resistivity measurements were made by four-point probe on the sectioned surfaces of the silicon droplets to obtain information on the influence of substrate contaminants. Approximate resistivity values are also given in Table 1 for those cases where the molten silicon was not totally absorbed by the substrate. The resistivity of the silicon used was nominally about 1000  $\Omega$ -cm. All substrates were cleaned and degreased prior to these tests. As expected, none of the materials examined were inert chemically to molten silicon or free from contamination effects. The materials which exhibited the most useful properties were reaction-sintered  $\text{Si}_3\text{N}_4$ , sintered  $\text{ZrO}_2$ , and vitreous carbon. Hot-pressed  $\text{Si}_3\text{N}_4$  displayed less desirable properties than reaction-sintered material in that there was evolution of more impurities from this material at high temperature. Boron-containing materials such as BN and  $\text{LaB}_6$  displayed only slight apparent reaction with molten silicon but proved to be strong sources of boron dopant.

##### B. SESSILE DROP EXPERIMENTS WITH CVD MATERIALS

The results of sessile drop experiments conducted on CVD SiC, CVD  $\text{Si}_3\text{N}_4$ , and CVD  $\text{SiO}_x\text{N}_y$  are also presented in Table 1 for comparison purposes. It can be seen that, with the exception of CVD SiC, the resistivity of the silicon benefits from the presence of the CVD coatings on the substrates, even when the CVD layer was cracked, as in the case of

TABLE 1. DATA FROM SESSILE DROP TESTS

<u>Material</u>	<u>Si Resistivity</u> <u><math>\Omega</math>-cm</u>	<u>Comments</u>
TiC (HP <sup>*</sup> )	--	porous, Si absorbed, reacted interfacial layer
ZrC (HP)	--	porous, Si absorbed
HfC (HP)	--	porous, Si absorbed
TaC (HP)	--	reacted with Si completely
TiN (HP)	--	deep penetration of Si in TiN and formation of another phase in Si
ZrN (HP)	too low to measure	deep penetration of Si with formation of reaction zone in ZrN
AlN (HP)	too low to measure	deep penetration of Si with possible formation of another phase along the boundary region of Si
AlN + 5% SiC (HP)	too low to measure	particulate erosion with precipitation in Si of a crystalline phase, possibly SiC
Si <sub>3</sub> N <sub>4</sub> (reaction sintered)	0.2	particulate erosion with formation of blocky crystals in Si
TiO <sub>2</sub> (conventionally sintered)	too low to measure	extensive reaction
ZrO <sub>2</sub> (conventionally sintered)	0.2	penetration of Si with probable formation of another phase in ZrO <sub>2</sub>
HfO <sub>2</sub> (single crystal)	too low to measure	formation of another phase in Si along boundary with HfO <sub>2</sub>
ThO <sub>2</sub> (HP)	too low to measure	slight penetration of Si and formation of eutectic phase in Si
LaB <sub>6</sub> (HP)	too low to measure	no apparent reaction
MoSi <sub>2</sub> (HP)	--	Si absorbed
Vitreous carbon	0.8	interfacial phase formed
CVD Si <sub>3</sub> N <sub>4</sub> on vitreous carbon	8.4	CVD layer cracked, Si penetration at cracks
CVD SiC	too low to measure	interfacial reaction with formation of another phase, probably SiC
CVD Si <sub>3</sub> N <sub>4</sub> /RS <sup>†</sup> Si <sub>3</sub> N <sub>4</sub>	18-34	after 4 h at 1440°C
CVD SiO <sub>x</sub> N <sub>y</sub> /RS Si <sub>3</sub> N <sub>4</sub>	2.8-8	after 4 h at 1440°C
CVD SiO <sub>x</sub> N <sub>y</sub> /RS Si <sub>3</sub> N <sub>4</sub>	0.2-0.8	after 22 h at 1440°C

Note: The silicon used in these tests was "Hyper-Pure" material (from Dow Corning Corp.) with  $\rho > 1000 \Omega$ -cm. The duration of the sessile drop tests was 30 min in all cases except for the last three samples shown in the table. The resistivities shown here are approximate values.

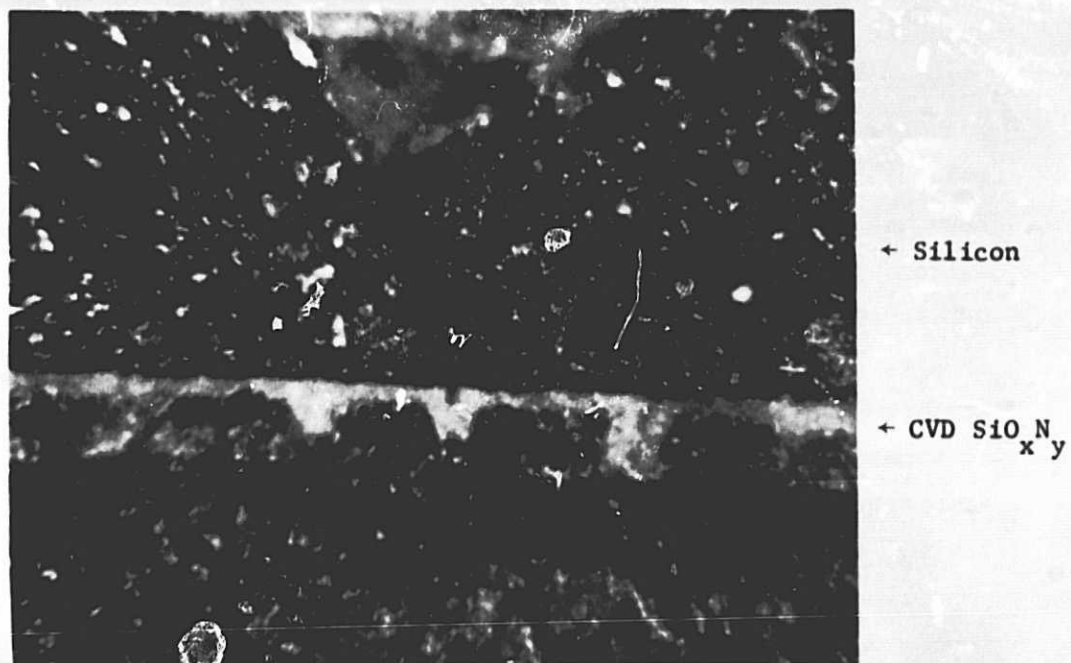
\* HP = hot pressed.

† RS = reaction sintered.

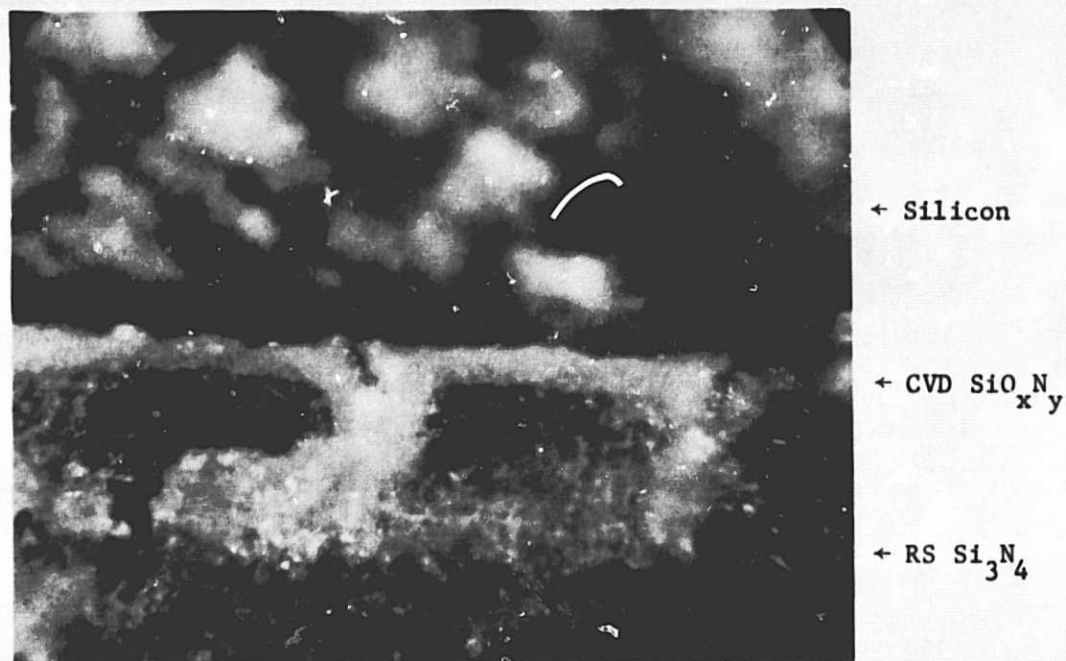
$\text{Si}_3\text{N}_4$  on vitreous carbon. In addition, these layers are capable of withstanding prolonged exposure to molten silicon as shown by the last three entries in Table 1. The stability of these CVD layers to molten silicon was discussed in Quarterly Report No. 4 of Contract No. 954465. Briefly, both CVD  $\text{Si}_3\text{N}_4$  and CVD  $\text{SiO}_x\text{N}_y$  act as useful barriers to impurity diffusion from the substrate in addition to considerable inertness in contact with molten silicon. There is also evidence from these experiments that the CVD layers tend to seal surface pores in the substrate material as shown in Fig. 1. The composition of the  $\text{SiO}_x\text{N}_y$  layers used here is not known at this time, but the atomic ratio of oxygen and nitrogen is expected to be about one. This, however, is the expected ratio at the deposition temperature of about  $1000^\circ\text{C}$  when the layers are amorphous. Subsequent heating to the melting point of silicon causes crystallization with possible change in composition occurring at the same time. This will be investigated further.

The silicon nitride and oxynitride layers discussed above were prepared by the reaction between ammonia and silane using the ratio  $\text{NH}_3:\text{SiH}_4 = 100:1$ . It has been generally recognized in the semiconductor literature that amorphous  $\text{Si}_3\text{N}_4$  films prepared with a ratio less than the above value are silicon-rich in composition, and some vendors supply these reagents, premixed at this ratio, for the deposition of CVD  $\text{Si}_3\text{N}_4$ . The cost of ammonia (5 nines purity) at this ratio, however, represents 90% of the estimated cost of depositing these layers in a production facility. Consequently, a reduction in this ratio could mean a substantial reduction in cost, provided the rate of erosion in contact with molten silicon is not seriously affected. We have prepared CVD  $\text{Si}_3\text{N}_4$  layers on vitreous carbon at the following ammonia to silane ratios, 33:1, 20:1, 10:1, and 5:1, and performed a preliminary evaluation of the layers in sessile drop experiments. Section micrographs of samples corresponding to the latter three ratios (after heating at  $1440^\circ\text{C}$  for about one hour) are shown in Figs. 2-4. No noticeable change in erosion rate was observed as a result of going from a ratio of 100:1 to 33:1. Consequently, this latter ratio has been used in the coating of dies for the growth of silicon ribbon. A section view of such a die after silicon ribbon growth is shown in Fig. 5. It appears from the limited number of samples studied at the lower ratios that it may be possible to coat





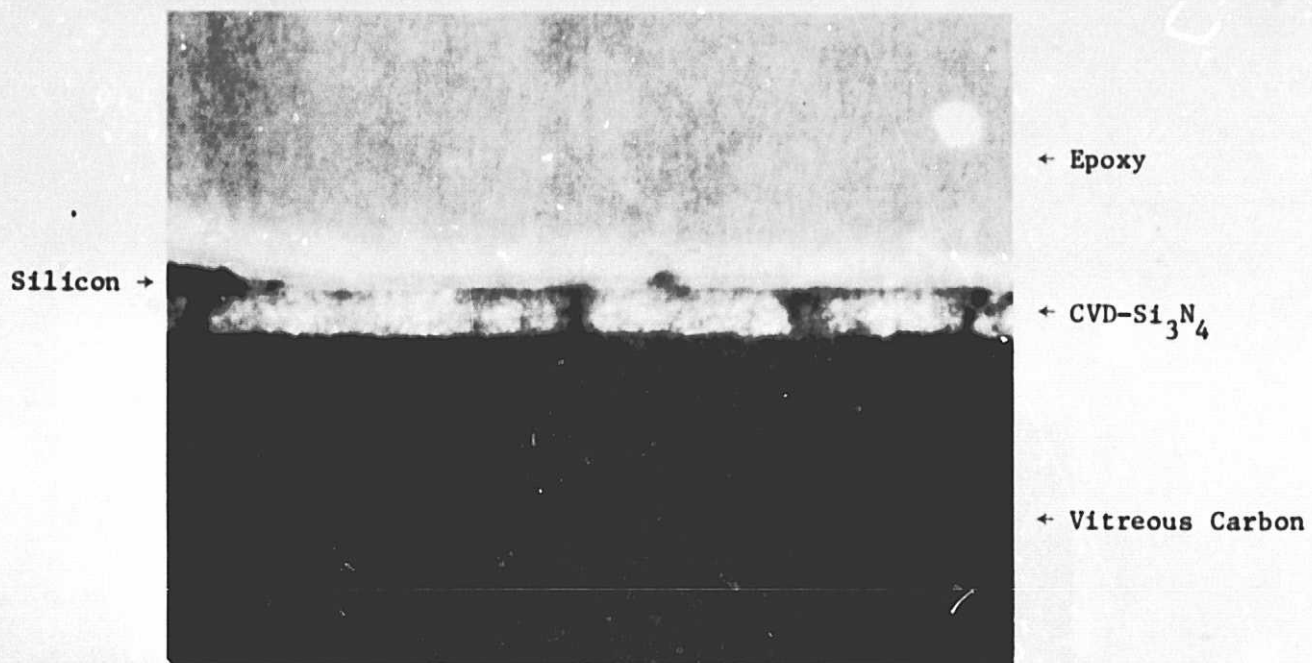
(a) CVD SiO<sub>x</sub>N<sub>y</sub>/RS Si<sub>3</sub>N<sub>4</sub> (~260X)



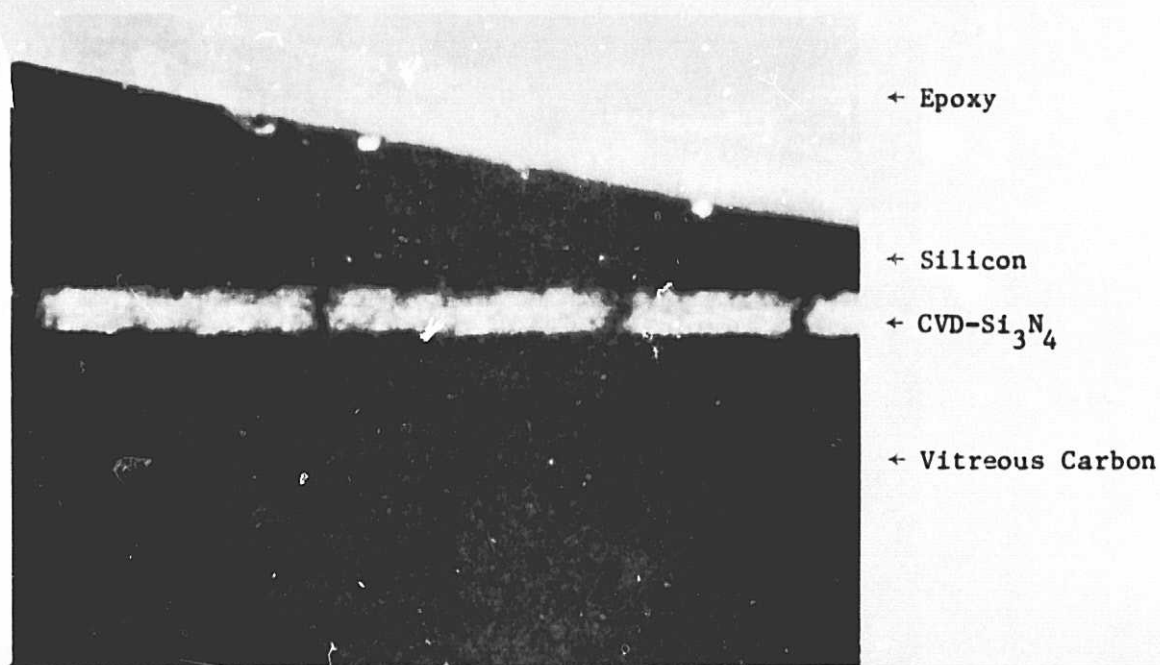
(b) CVD SiO<sub>x</sub>N<sub>y</sub>/RS Si<sub>3</sub>N<sub>4</sub> (~680X)

**Figure 1.** Photograph of a sectioned Si/CVD SiO<sub>x</sub>N<sub>y</sub>/RS Si<sub>3</sub>N<sub>4</sub> sample showing evidence of CVD layer filling pores in surface of substrate: (a) ~260X, (b) same region at higher magnification ~680X.





(a)  $\sim 300X$



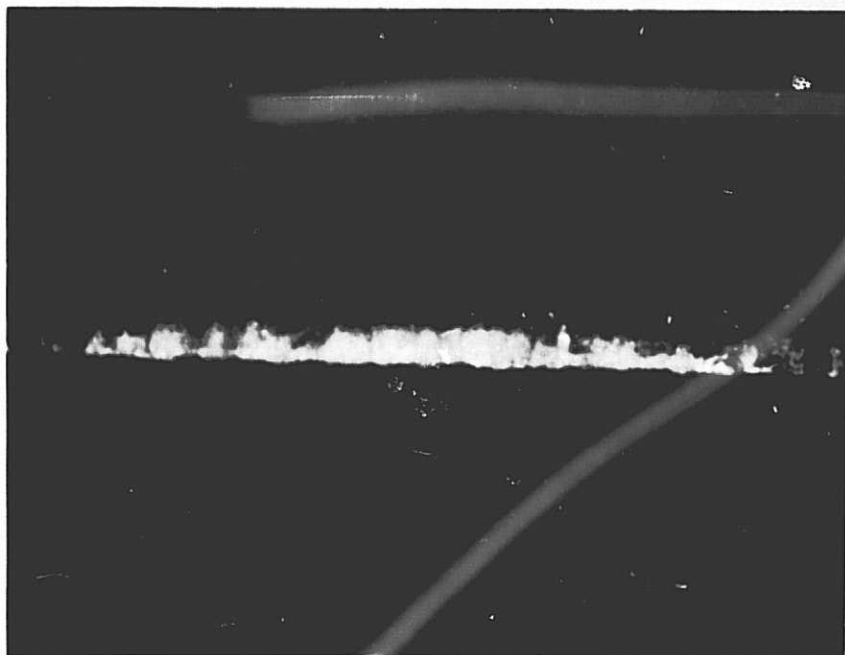
(b)  $\sim 300X$

**Figure 2.** Section micrographs of Si/CVD  $Si_3N_4$ /vitreous carbon composite, (a) at edge of silicon droplet, (b) under silicon droplet. Cracking of CVD layer due to thermal expansion mismatch is evident.  $NH_3:SiH_4 = 20:1$ .

Epoxy →



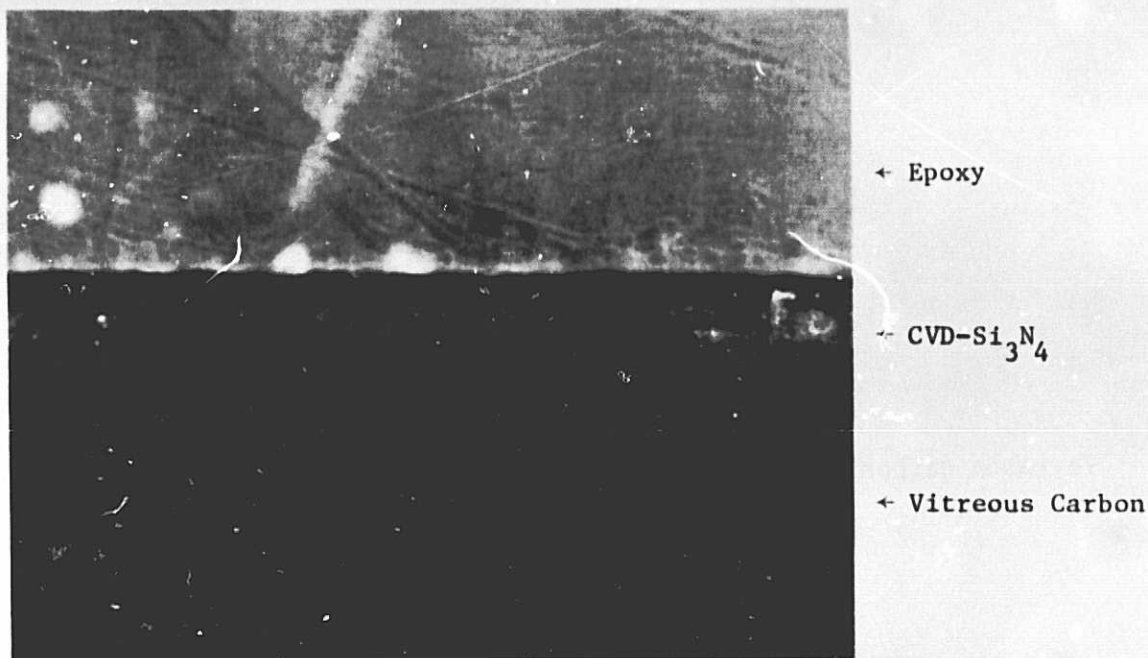
(a) ~300X



(b) ~300X

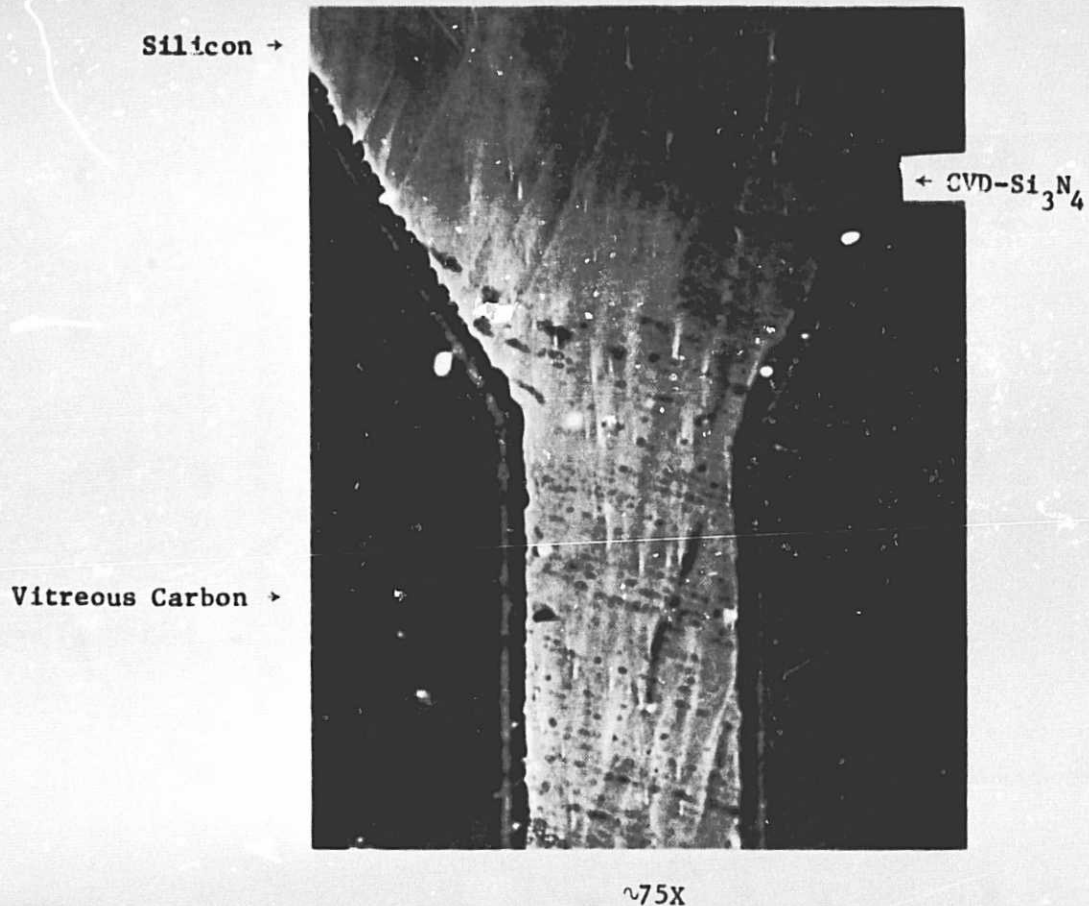
Figure 3. Section micrographs of Si/CVD Si<sub>3</sub>N<sub>4</sub>/vitreous carbon composite, (a) at edge of silicon droplet, (b) under silicon droplet. NH<sub>3</sub>:SiH<sub>4</sub> = 10:1.

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~300X

Figure 4. Section micrograph of Si/CVD Si<sub>3</sub>N<sub>4</sub>/vitreous carbon after experiment. Silicon droplet has disappeared down edges of substrate. NH<sub>3</sub>:SiH<sub>4</sub> = 5:1.



~75X

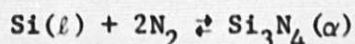
**Figure 5.** Section photograph of CVD coated die after ribbon growth experiment.  $\text{NH}_3:\text{SiH}_4 = 33:1$ .



dies at these lower ratios without appreciably altering the useful life of the dies during ribbon growth. At a ratio of  $\text{NH}_3:\text{SiH}_4 = 5:1$  the wetting characteristics of the CVD layer may have changed to lower a contact angle in that the molten silicon droplet spread across the surface and down the edges of the CVD coated substrate. This is being studied further.

### C. THERMAL STABILITY OF CVD $\text{Si}_3\text{N}_4$ FILMS

It appears from previous work [1,2] that the equilibrium partial pressure of  $\text{N}_2$  associated with the reaction



at the melting point of silicon is about 1 torr. This value obtained on  $\alpha\text{-Si}_3\text{N}_4$  seems higher than might be inferred from our observations on the stability of CVD  $\beta\text{-Si}_3\text{N}_4$  near the melting point of silicon. A set of experiments is in progress to obtain information on the decomposition of the CVD layers near the melting point of silicon. The first of these involves depositing a thin ( $\sim 1000 \text{ \AA}$ )  $\text{Si}_3\text{N}_4$  film on a polished silicon substrate and heating such a sample to below the melting point of silicon in ultrapure He for a suitable period of time. Because the color of films in this thickness region is a sensitive function of film thickness [3,4], it should be possible to observe small changes ( $\sim 100 \text{ \AA}$ ) in film thickness or the possible disappearance of the film after temperature cycling. Color comparisons were made on two portions of each sample, one of which was heat treated for about 30 min while the other portion was left untreated. No noticeable change in color was observed for heat treatments to  $1300^\circ\text{C}$ . At  $1400^\circ\text{C}$ , a discoloration or hazy film appearance was observed due to pitting of the silicon surface. However, the original film tint was still visible, and when the samples were immersed in silicon etchant ( $\text{HNO}_3 + \text{HF}$ ), an insoluble film remained.

1. R. D. Pehlke and J. F. Elliott, "High-Temperature Thermodynamics of the Silicon, Nitrogen, Silicon Nitride System," AIME Trans. 215, 781 (1959).
2. W. B. Hincke and L. R. Brantley, "The High-Temperature Equilibrium Between Silicon Nitride, Silicon, and Nitrogen," J. Am. Chem. Soc. 52, 48 (1930).
3. W. A. Pliskin and E. E. Conrad, "Nondestructive Determination of Thickness and Refractive Index of Transparent Films," IBM Journal 8, 43 (1964).
4. F. Reizman and W. van Gelder, "Optical Thickness Measurement of  $\text{SiO}_2\text{-Si}_3\text{N}_4$  Films on Silicon," Solid-State Electron. 10, 625 (1967).

Figure 6 is a micrograph of a CVD  $\text{Si}_3\text{N}_4/\text{Si}$  composite after heating to about  $1405^\circ\text{C}$  for one hour followed by etching in silicon etchant. The photograph was taken while the sample was still immersed in solution and shows the CVD film folded away from the edge of the sample as a result of undercutting the silicon from under the film (right-hand side of the micrograph). It appears from these initial experiments that the decomposition rate of CVD  $\text{Si}_3\text{N}_4$  near the melting point of silicon is not more than  $100 \text{ \AA/h}$ .

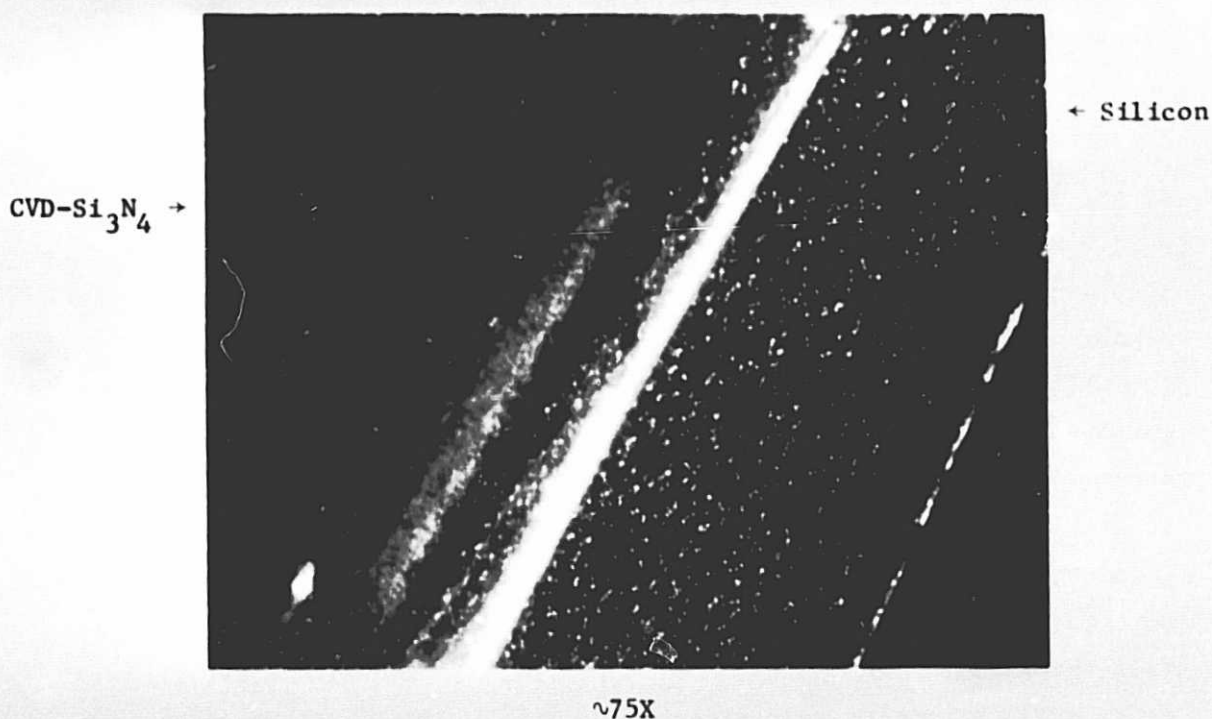


Figure 6. Surface photograph of CVD  $\text{Si}_3\text{N}_4/\text{Si}$  sample after heating at  $1405^\circ\text{C}$  for 1 h and etching in  $\text{HF} + \text{HNO}_3$  acid mixture. The thin ( $\sim 1000 \text{ \AA}$ ) nitride film has curled over from the edge of the substrate as a result of undercutting in the etchant (right-hand side of photograph) and is visible because of reflection from the curved surface of the curled film.  $\text{NH}_3:\text{SiH}_4 = 33:1$ .

#### D. SILICON RIBBON GROWTH

Several silicon ribbon growth runs, using the V-shaped die configuration, were performed during this reporting period. The most successful of these utilized vitreous carbon dies coated with CVD  $\text{Si}_3\text{N}_4$  using the  $\text{NH}_3:\text{SiH}_4 = 33:1$  ratio as described previously. In all cases the vitreous carbon pieces were "fired" in HCl gas at about  $1500^\circ\text{C}$  prior to  $\text{Si}_3\text{N}_4$  deposition on the side in contact with the silicon melt. There was a dramatic difference in the resistivity of silicon ribbon specimens grown from the different dies depending upon the purity and origin of the substrate material. Resistivity values ranged from  $10^{-2} \Omega\text{-cm}$  to about  $40 \Omega\text{-cm}$ . Vitreous carbon is known to have a relatively high concentration of boron, which varies with the vendor. The ribbon segments grown from CVD  $\text{Si}_3\text{N}_4$  coated vitreous carbon dies were invariably p-type material.



## SECTION IV

### CONCLUSIONS AND FUTURE PLANS

Evaluation of the reactivity of molten silicon with CVD  $\text{Si}_3\text{N}_4$  and CVD  $\text{SiO}_x\text{N}_y$  indicates that these materials are considerably more resistant to chemical attack than many of the refractory carbides, nitrides, and oxides commercially available at the present time. Simultaneously, these layers provide a useful barrier to impurity diffusion from the substrate material into the molten silicon. The cleanest substrate material examined to date has been vitreous carbon, and silicon ribbon segments with resistivity up to  $40 \Omega\text{-cm}$  have been grown from vitreous carbon dies coated with CVD  $\text{Si}_3\text{N}_4$ .

The thermal stability of CVD  $\text{Si}_3\text{N}_4$  near the melting point of silicon appears to be better than that reported in the literature for sintered  $\text{Si}_3\text{N}_4$ . Preliminary experiments on thin films indicate that the rate of decomposition is less than  $100 \text{ \AA/h}$  at temperatures a few degrees below the melting point of silicon. The cost of preparing CVD layers is strongly dependent upon the  $\text{NH}_4:\text{SiH}_4$  ratio used in the deposition process. A substantial reduction in cost can be attained by lowering this ratio if the integrity of the layers is not degraded. Our initial experiments indicate that significant cost savings can be attained in this manner.

We plan to continue with the evaluation of CVD layers in both silicon sessile drop experiments and in die applications for the growth of silicon ribbon. Greater emphasis in the next quarter will be placed on layer morphology and microstructure and on suitable substrate materials. The plan is to continue according to the milestones schedule in Appendix C.



## REFERENCES

1. R. D. Pehlke and J. F. Elliott, "High-Temperature Thermodynamics of the Silicon, Nitrogen, Silicon Nitride System," AIME Trans. 215, 781 (1959).
2. W. B. Hincke and L. R. Brantley, "The High-Temperature Equilibrium Between Silicon Nitride, Silicon, and Nitrogen," J. Am. Chem. Soc. 52, 48 (1930).
3. W. A. Pitskin and E. E. Conrad, "Nondestructive Determination of Thickness and Refractive Index of Transparent Films," IBM Journal 8, 43 (1964).
4. F. Reizman and W. van Gelder, "Optical Thickness Measurement of  $\text{SiO}_2$ - $\text{Si}_3\text{N}_4$  Films on Silicon," Solid-State Electron. 10, 625 (1967).

**APPENDIX A**

**SECTION MICROGRAPHS FROM SESSILE DROP TESTS  
REFERRED TO IN TABLE 1**

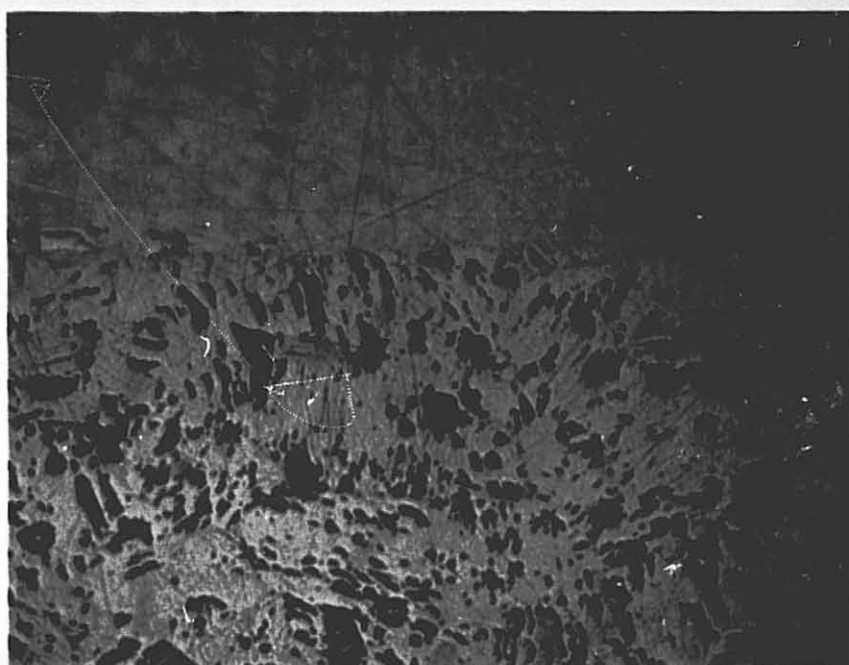


← Silicon

← Reaction  
Zone

← TiC

TiC (~550X)



← Silicon

← Silicon  
in TiN

TiN (~550X)





← Silicon

← Reaction  
Zone

← ZrN

ZrN (~550X)

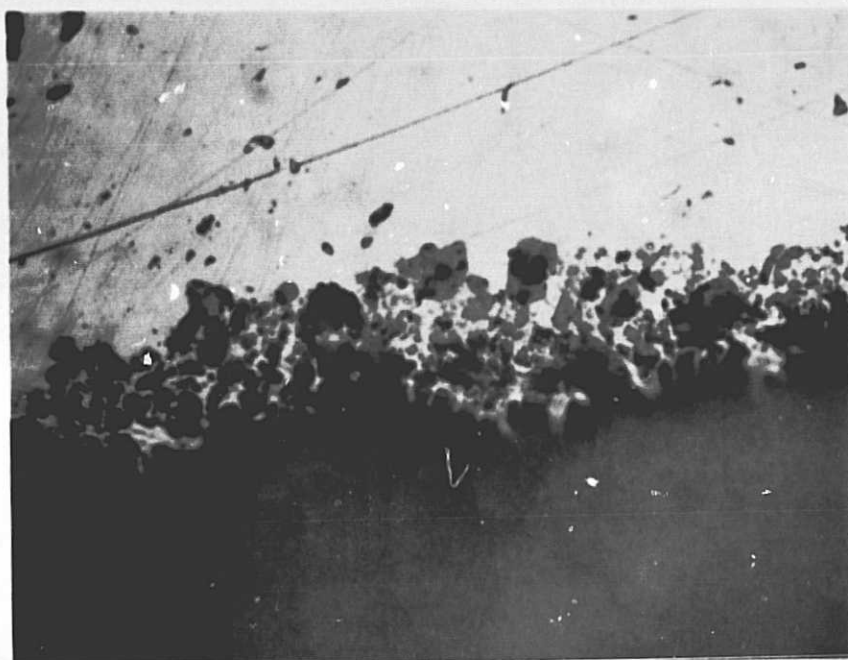


← Silicon

← AlN

Silicon in →  
AlN

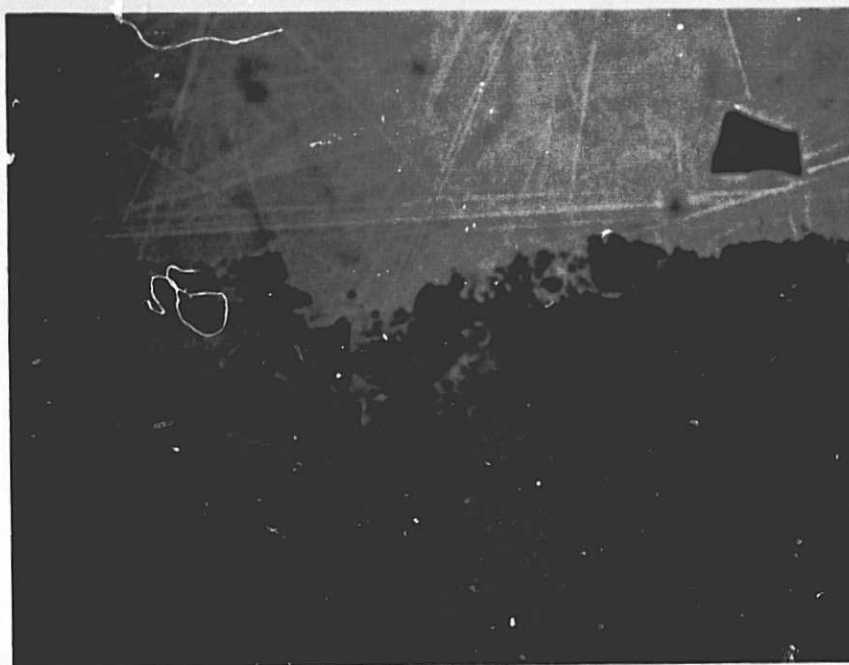
AlN (~100X)



← Silicon

← AlN + SiC

AlN + 5% SiC (~550X)



← Silicon

← RS Si<sub>3</sub>N<sub>4</sub>

RS Si<sub>3</sub>N<sub>4</sub> (1080X)



← Silicon

←  $\text{ZrO}_2$

$\text{ZrO}_2$  (~550X)



← Silicon

$\text{HfO}_2$

$\text{HfO}_2$  (215X)

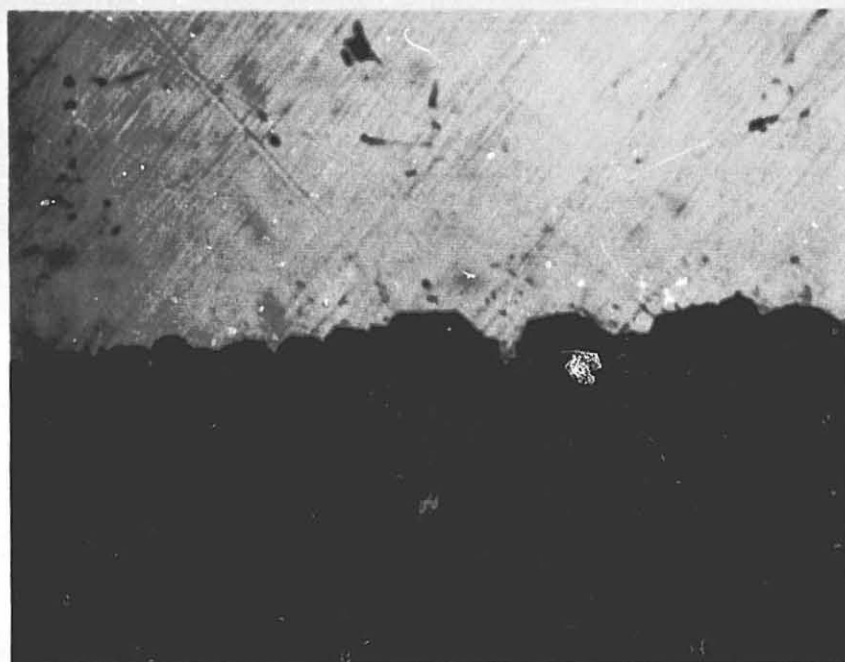




← Silicon

← ThO<sub>2</sub>

ThO<sub>2</sub> (~550X)



← Silicon

← LaB<sub>6</sub>

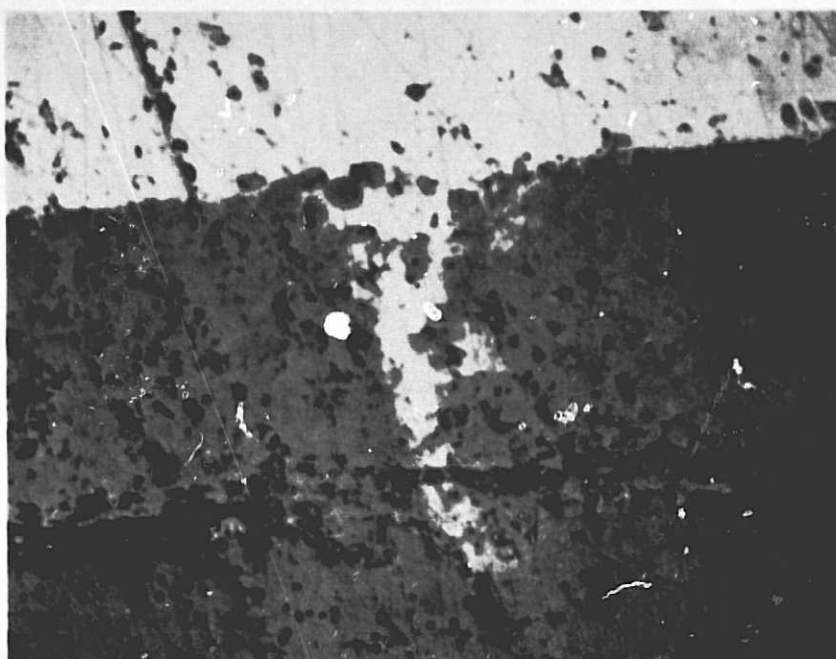
LaB<sub>6</sub> (~550X)



← Silicon

← Vitreous Carbon

Vitreous Carbon ( $\sim 550\times$ )



← Silicon

← CVD  $\text{Si}_3\text{N}_4$

← Vitreous Carbon

CVD  $\text{Si}_3\text{N}_4$ /Vitreous Carbon ( $\sim 550\times$ )



← Silicon

← CVD SiC

CVD SiC (~550X)



**APPENDIX B**  
**NEW TECHNOLOGY**

**There are no new technology items for this reporting period.**

## MILESTONES FOR DIE AND CONTAINER DEVELOPMENT

1. Development and Evaluation of CVD  $\text{Si}_3\text{N}_4$ - $\text{SiO}_x\text{N}_y$  Systems
  - degradation and erosion rate of CVD  $\text{Si}_3\text{N}_4$  in contact with molten Si
  - optimization of CVD  $\text{Si}_3\text{N}_4$  as related to preparative conditions and post-deposition annealing
  - composition of as-deposited CVD  $\text{SiO}_x\text{N}_y$  layers and identification of phases present after crystallization, above the melting point of Si
  - degradation and erosion rate of CVD  $\text{SiO}_x\text{N}_y$  in contact with molten Si
  - optimization with respect to preparative and annealing conditions
  - deposit above CVD layers on various die materials for the growth of silicon ribbon
  - fabricate self-supporting CVD dies and crucibles and test in contact with molten Si
2. Evaluation of Other CVD Coatings
  - identify other potentially useful coatings
  - prepare CVD coatings
  - test erosion in contact with molten Si
3. Reaction and Pressure-Sintered Materials for Use as CVD Substrates
  - $\text{Si}_3\text{N}_4$  with various densification aids
  - $\text{SiO}_x\text{N}_y$
  - Mullite
4. Characterization
  - materials characterization studies will be conducted according to that outlined in Articles 1 and 2 of Task Order No. RD-152
5. Inverted Ribbon Growth w/CVD Dies
  - Growth Rate
    - 50 cm/h
    - 100 cm/h
    - 150 cm/h
    - 200 cm/h
  - Thickness ( $\pm$  5 mil)
    - 40 mil
    - 30 mil
    - 20 mil
    - 15 mil
  - Ribbon Length (cm)
    - 10 cm
    - 15 cm
    - 20 cm
    - 30 cm
  - Operation of Mark I Puller
  - Operation of Mark II Puller

[illegible]

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## APPENDIX D

### MANHOURS AND COSTS

Manhours and cost totals for the months of October and November were 846 and \$30,500, respectively.